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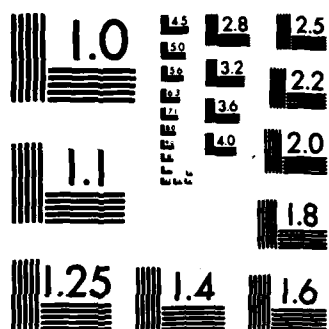
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MAGNETIC EXCHANGE INTERACTIONS IN THE LINEAR CHAIN CHROMIUM(III)
COMPOUNDS CATENA-FLUOROPHTHALOCYANINATOCHROMIUM(III) AND
CATENA-CYANOPHTHALOCYANINATOCHROMIUM(III)

BY

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theory for ferromagnetic exchange with $J = 0.2/\text{cm}^2$ and $g = 1.98$. $[\text{CrPcCN}]_n^7$ provides the first example of ferromagnetic exchange in a linear chain of chromium(III) ions. The difference in the exchange interactions in $[\text{CrPcF}]_n^7$ and $[\text{CrPcCN}]_n^7$ may be understood in terms of the electronegativities of the bridges and in terms of the orbitals which transmit the superexchange interactions. Originator Supplied Keywords include:

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Contribution from the Department of Chemistry
The University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27514

**Magnetic Exchange Interactions in the Linear Chain
Chromium(III) Compounds**

**Catena-fluorophthalocyaninatochromium(III) and
Catena-cyanophthalocyaninatochromium(III)**

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Received

Abstract

Magnetic susceptibility and magnetization studies on the linear chain chromium(III) compounds catena-fluorophthalocyaninatochromium(III), $[\text{CrPcF}]_n$, and catena-cyanophthalocyaninatochromium(III), $[\text{CrPcCN}]_n$, reveal that the chromium(III) ions in $[\text{CrPcF}]_n$ and $[\text{CrPcCN}]_n$ are magnetically exchange coupled. The magnetic susceptibility data for $[\text{CrPcF}]_n$ may be fit with Heisenberg linear chain theory for antiferromagnetic exchange with $J = -12.2 \text{ cm}^{-1}$ and $g = 2.00$. The magnetic susceptibility data for $[\text{CrPcCN}]_n$ may be fit with Heisenberg linear chain theory for ferromagnetic exchange with $J = 0.2 \text{ cm}^{-1}$ and $g = 1.98$. $[\text{CrPcCN}]_n$ provides the first example of ferromagnetic exchange in a linear chain of chromium(III) ions. The difference in the exchange interactions in $[\text{CrPcF}]_n$ and $[\text{CrPcCN}]_n$ may be understood in terms of the electronegativities of the bridges and in terms of the orbitals which transmit the superexchange interactions.

Introduction

There have been few studies of magnetic exchange interactions in linear chain chromium(III) compounds.² The reason for the lack of attention to this important fundamental problem may be traced to the paucity of chromium(III) compounds with linear chain structures. Six-coordinate, quasi-octahedral chromium(III) has a 4A ground state, and typically, the zero-field splitting of the 4A state in such complexes is small.³ As a result, Heisenberg exchange theory as described by the Hamiltonian

$$H = -2J \sum_{i=1}^{N-1} \hat{S}_i \cdot \hat{S}_{i+1}$$

is expected to be applicable.

Weng⁴ has provided the necessary results for the analysis of experimental data for antiferromagnetically exchange coupled linear chains of $S = 3/2$ ions, and Smith and Friedberg⁵ have given a scaled version of the infinite spin Heisenberg linear chain theory derived by Fisher⁶ that is useful for ferromagnetically exchange coupled chains. In addition, a convenient, closed-form expression for the magnetic susceptibility of antiferromagnetically exchange-coupled $S = 3/2$ ions has been reported.⁷

Perhaps the most thoroughly studied series of chromium(III) chains are compounds with the general formula $ACrF_4$ ($A^+ = Na^+, K^+, Rb^+, \text{ and } Cs^+$).⁸ These compounds have a triple chain structure,⁹ and a Hamiltonian with nearest neighbor, and next-nearest neighbor exchange is required for a precise analysis of the magnetic susceptibility data. Babel and coworkers¹⁰ have shown that there is a correlation between the diminution of the magnetic moment and the M-F-M angle in fluoro-

bridged chromium chains including the mono- μ -fluoro-bridged chain in BaCrF_5 . Extensive studies have been carried out on a series of polychromiumphosphinate polymers of the general formula $[\text{Cr}(\text{O}_2\text{PR}_i\text{R}_j)_3]_n$ (R_i and R_j are alkyl groups), and these have been found to exhibit a variety of properties including random antiferromagnetic exchange,¹¹ anisotropy, and magnetic field dependence.¹² These polymers have three $^-\text{O}-\text{P}(\text{R}_1\text{R}_2)-\text{O}^-$ bridges.

It has long been supposed that the compound $[\text{CrPcF}]_n$ had a fluoro-bridged, linear chain structure.¹³ New magnetic susceptibility that support that view are presented here.

As a part of a program devoted to the production of new compounds with high electrical conductivities, the linear chain compound $[\text{CrPcCN}]_n$ was synthesized and characterized.¹⁴ Magnetic susceptibility and magnetization measurements presented here reveal that the chromium(III) ions exhibit ferromagnetic intrachain exchange interactions. Ferromagnetic intrachain interactions in linear-chain chromium(III) compounds, or other $S = 3/2$ ions, appear not to have been observed previously.

Experimental Section

Catena-fluorophthalocyaninatochromium(III) was obtained from Eastman Kodak. Magnetic susceptibility studies revealed the presence of paramagnetic impurities in $[\text{CrPcF}]_n$ as evidenced by a Curie-like tail, and attempts were made to purify the sample by Soxhlet extraction with ethanol and by vacuum sublimation. Proper conditions for the complete removal of the paramagnetic impurity were not found.

Phthalocyaninatochromium(III) was prepared by the method of Meloni and Block.¹⁵

Preparation of $\text{Na}[\text{PcCr}(\text{CN})_2] \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$.¹⁶ PcCr (0.56 g, 1 mmol) and NaCN (1.47 g, 3 mmol) were suspended under nitrogen in ethanol (40 mL) at room temperature. The resulting solution was filtered through a glass frit to remove the unreacted PcCr . The product was precipitated from this solution as dark green needles by blowing air over it for 1 min. Three days later the hygroscopic crystals were filtered, washed with petroleum ether (30–50°C) and dried in vacuo at room temperature; yield 0.59 g (82%). Anal. Calcd for $\text{C}_{36}\text{H}_{26}\text{N}_{10}\text{O}_3\text{CrNa}$: C, 59.92; H, 3.63; N, 19.37. Found: C, 59.94; H, 3.46; N, 19.37. IR (Nujol): 2133 cm^{-1} ($\text{C}=\text{N}$).

Preparation of $[\text{PcCrCN}]_n$.¹⁶ $[\text{PcCrCN}]_n$ was prepared analogous to $[\text{PcCoCN}]_n$ ¹⁷ by extracting $\text{Na}[\text{PcCr}(\text{CN})_2]$ with water for 2 days in a Soxhlet extractor. The resulting greenish-black powder was dried in vacuo. $[\text{PcCrCN}]_n$ contains about 1 mol of water per PcCrCN unit. The X-ray powder pattern is identical with that of $[\text{PcCoCN}]_n$. Anal. Calcd for $\text{C}_{33}\text{H}_{18}\text{N}_9\text{OCr}$: C, 65.13; H, 2.98; N, 20.71. Found: C, 64.59; H, 2.90; N, 20.31. IR (Nujol): 2150 cm^{-1} ($\text{C}=\text{N}$).

Magnetic susceptibility and magnetization data were collected with a vibrating sample magnetometer as described previously.¹⁸ A diamagnetic correction of -2.34×10^{-4} was used for the phthalocyanine ligand since this is the measured value of the magnetic susceptibility of nickel phthalocyanine.¹⁹ Pascal's constants were used for the diamagnetic correction of the other constituents.²⁰

Electrical conductivities of pressed pellets of $[\text{CrPcF}]_n$ were measured to be $<10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ using a conventional four-probe technique, a Keithley 227 constant current source, and a Fluke 8502A multimeter.

Results

Magnetic Properties of $[\text{CrPcF}]_n$. The magnetic susceptibility of $[\text{CrPcF}]_n$ was measured in the temperature range 4.2 to 225 K in an applied magnetic field of 10 kOe on several samples. The high temperature (>20 K) behavior of all samples were in good agreement, but the low temperature data varied as a result of paramagnetic impurities and chain-end effects. The magnetic moment data presented in Figure 1 were collected on a sample of $[\text{CrPcF}]_n$ as obtained from Eastman Kodak.

The temperature dependence of an antiferromagnetically exchange coupled $S = 3/2$ chain is given by the polynomial expression in Equation (1),

$$\chi_{\text{chain}} = \frac{Ng^2\mu_B^2}{kT} \times \frac{A(S) + B(S)x^2}{1 + C(S)x + D(S)x^3} \quad (1)$$

where $x = |J|/kT$ and the constants $A(S)$, $B(S)$, $C(S)$, and $D(S)$ have the values 1.25, 17.041, 3.736, and 238.47, respectively.⁷ The presence of monomeric impurities in the observed magnetic susceptibility may be accounted for by assuming that $\chi_{\text{obsd}} = \chi_{\text{chain}} + \chi_{\text{impurity}}$. Furthermore, by assuming that the impurity obeys the Curie Law, the following expression for the total susceptibility results:²¹

$$\chi_{\text{obsd}} = \left\{ \frac{PNg^2\mu_B^2S(S+1)}{3k} + (100 - P)\chi_{\text{chain}} \right\} / 100 \quad (2)$$

where $S = 3/2$, P = the percent impurity, and g is set equal to the value for the chain. Chain-end effects will make the same kind of contribution to the magnetic susceptibility as monomeric impurities, and it is not possible to distinguish between them. Equation (2) was fit to the experimental data using a non-linear Simplex least squares fitting routine,²²

with the criterion of best fit being the minimum value of the function

$$F = \sum_i \frac{(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2}{\chi_i^{\text{obsd}}}$$

As shown in Figure 1, a good fit of the temperature variation of the magnetic moment, $\mu_{\text{eff}} = 2.828(\chi_{\text{obsd}} \cdot T)^{\frac{1}{2}}$, is given by the best fit of Equation (2) to the data and the parameters $J = -12.2 \text{ cm}^{-1}$, $g = 2.00$, and 5.9% impurity.

It is also possible to fit the experimental data assuming pairwise exchange between two $S = 3/2$ ions. The best fit of Equation (3) to the experimental data yielded the best-fit parameters $J = -19.2 \text{ cm}^{-1}$, $g = 1.98$, and $P = 3.3\%$ with the biquadratic exchange coupling constant j held constant at 0.0. The temperature variation of the magnetic moment obtained with these parameters is shown in Figure 1.

$$\chi_M = \frac{Ng^2\mu_B^2}{kT} \times \frac{\{2.0\exp[(2J-6.5j)/kT] + 10.0\exp[(6J-13.5j)/kT] + 28.0\exp[(12J-9j)/kT]\}}{(1 + 3.0\exp[(2J-6.5j)/kT] + 5.0\exp[6J-13.5j)/kT] + 7.0\exp[(12J-9j)/kT])} \quad (3)$$

In principle, low temperature magnetic susceptibility data will permit differentiation between chains and dimers. Unfortunately, in this case, the paramagnetic impurity obscures the low temperature magnetic behavior of $[\text{CrPcF}]_n$ and does not permit the differentiation.

Magnetic Properties of $[\text{CrPcCN}]_n$. The magnetic susceptibility of $[\text{CrPcCN}]_n$ was measured over the temperature range 2.0 to 95 K in an applied magnetic field of 10.0 kOe. Since the magnetic moment increased from 3.88 B. M. at high temperatures to 4.7 B. M. at the low temperature end of the measurements, it was concluded that ferromagnetic interactions were present. Therefore, the magnetization of $[\text{CrPcCN}]_n$ was measured in the field range 50-12,000 Oe at 4.2 K and in the range 250-12,000 Oe at 2.4 K. The data are given in Figure 3.

The temperature variation of the magnetic susceptibility and magnetic moment of $[\text{CrPcCN}]_n$ may be fit by the expression [Equation (4)] for an exchange coupled Heisenberg infinite-spin linear chain⁶ which has been scaled to $S = 3/2$.⁵

$$\chi_{\text{chain}} = \frac{Ng^2\mu_B^2 S(S+1)}{kT} \times \frac{1 + \coth(x) - 1/x}{1 - \coth(x) - 1/x} \quad (4)$$

In Equation (4), $x = 2JS(S+1)/kT$. The solid lines in Figure 2 were generated with $\mu_{\text{eff}} = 2.828(\chi_{\text{chain}} \cdot T)^{1/2}$ and the best least-squares fit magnetic parameters $J = 0.18 \text{ cm}^{-1}$ and $g = 1.98$. However, as shown in Figure 2, the equation for pairwise exchange in an $S = 3/2$ dimer is also capable of fitting the

temperature variation of the magnetic moment. The best least-squares values of the magnetic parameters obtained by fitting Equation (3) to the magnetic data for $[\text{CrPcCN}]_n$ are $J = 0.44 \text{ cm}^{-1}$ and $g = 1.98$. In these fits, P and j were held constant at 0.0.

The magnetization data presented in Figure 3 provide additional evidence for extended ferromagnetic interactions. It may be seen that the magnetization data collected at 2.4 and 4.2 K and plotted as magnetic moment versus H/T are enhanced over the theoretical values calculated from the Brillouin function for $S = 3/2$. Additionally, the magnetic moments at 2.4 K are larger than those at 4.2 K at all corresponding values of H/T . These features are all indicative of ferromagnetic interactions.

It may be argued that the observed behavior arises from ferromagnetic impurities that have not ordered and that exhibit enhanced paramagnetic susceptibilities. We believe that this is unlikely in view of the smooth variation of the magnetic moment with temperature. Such smooth variations of magnetic moment with temperature are not given by simulations of magnetic susceptibility with a model consisting of an antiferromagnetically coupled chain [Equation (1)] and a ferromagnetic impurity with enhanced paramagnetic susceptibilities given by Equation (5).²³

$$\chi_{\text{ferro}} = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} \times \frac{4}{\exp(-2j') + 3 - 2(z-1)j'} \quad (5)$$

In Equation (5), $j' = J/kT$ and $z = 2$, the number of nearest neighbors. The magnetic susceptibility of a system consisting of antiferromagnetically coupled chains [Equation (1)] and a ferromagnetic impurity is given by

$$\chi_{\text{obsd}}' = \{P'\chi_{\text{chain}} + (100 - P')\chi_{\text{ferro}}\}/100 \quad (6)$$

It was not possible to fit Equation (6) to the observed magnetic susceptibility with any reasonable values of the magnetic parameters.

Discussion

Structure of $[\text{CrPcF}]_n$. The magnetic properties of the two compounds $[\text{CrPcF}]_n$ and $[\text{CrPcCN}]_n$ are consistent with linear chains of chromium(III) ions experiencing intrachain exchange coupling. The results of this study support previous suggestions¹³ that $[\text{CrPcF}]_n$ is a mono- μ -fluoro-bridged chain of $[\text{CrPc}]$ units. In such a chain, it is likely that the Cr-F-Cr bridge angle would be close to 180° , since the angle will be dictated by the packing of the $[\text{CrPc}]$ units. It is possible that a deviation from 180° could arise by a process similar to the displacement of the oxo-bridge in catena- μ -oxo-hemiporphyrizinatoiron(IV) from the iron-iron vector.⁷ The Fe-O-Fe angles are 158° and 171° in $[\text{FeOHp}]_n$.

Accepting the premise that the Cr-F-Cr bridge is near 180° , it is interesting to compare the exchange coupling constant of -12.2 cm^{-1} in $[\text{CrPcF}]_n$ with that of -2.5 cm^{-1} in BaCrF_5 ,¹⁰ which has a Cr-F-Cr angle of 137° . Babel and coworkers¹⁰ had noted earlier that antiferromagnetic exchange coupling is enhanced as the Cr-F-Cr angle increases. Unfortunately, it is not possible to compare exchange coupling constants for the systems now available, since some examples quoted in the comparison have structures that permit next-nearest neighbor, as well as nearest neighbor, exchange.

Structure of $[\text{CrPcCN}]_n$. The linear chain structure of $[\text{CrPcCN}]_n$ has been verified by several physical methods, especially by its spectral properties.¹⁴ For example, the $\text{C}\equiv\text{N}$ stretching vibration in $[\text{CrPcCN}]_n$ is shifted 17 cm^{-1} to higher energy than that observed in monomeric $\text{Na}[\text{PcCr}(\text{CN})_2]\cdot\text{EtOH}\cdot 2\text{H}_2\text{O}$. The increase in energy of the $\text{C}\equiv\text{N}$ stretching vibration of this magnitude is evidence of a cyano bridge. Statistically, the fit for the linear chain to the magnetic susceptibility data is better ($F = 7.7 \times 10^{-3}$ versus $F = 1.7 \times 10^{-2}$ for the dimer fit), and it is apparent from Figure 2 that the linear chain model fits the observed data better at the lowest temperatures. Also, it is difficult to formulate a dimeric structure based on the stoichiometry of the compound.

Exchange Coupling in the Linear Chains. The substitution of CN^- for F^- as the bridging ligand has a profound effect on the exchange coupling. The magnetic data for $[\text{CrPcCN}]_n$ are consistent with ferromagnetic intrachain exchange interactions with $J = +0.2\text{ cm}^{-1}$ while the exchange interactions are antiferromagnetic in $[\text{CrPcF}]_n$. Apparently, $[\text{CrPcCN}]_n$ is the first example of a chromium(III) or $S = 3/2$ chain compound to exhibit ferromagnetic intrachain exchange interactions. It is of interest to examine exchange coupling in $[\text{CrPcF}]_n$ and $[\text{CrPcCN}]_n$ in terms of the orbitals available for transmitting the superexchange interaction and the relative electron density distributions on the two ligands.

It is well known that the exchange coupling term J is a sum of two contributions, those being J_F , a ferromagnetic contribution, and J_{AF} , an antiferromagnetic contribution. It is clear that factors that contribute to J_F predominate in $[\text{CrPcCN}]_n$, while those that contribute to J_{AF} predominate in $[\text{CrPcF}]_n$. We shall now examine these in terms of the relative electron density distributions on the two ligands. First, the

fluoride ion is rather small, and the chromium(III)-chromium(III) separation is expected to be smaller in $[\text{CrPcF}]_n$ than in $[\text{CrPcCN}]_n$. Since exchange interactions vary as r_{ij}^{-n} , this factor alone will enhance contributions to J in $[\text{CrPcF}]_n$. However, it is necessary to examine the occupancy and orientations of the orbitals of the bridging ligand with respect to those of the metal orbitals in order to make comparisons of the relative magnitudes of the various contributions to the exchange coupling constant.

Exchange in $[\text{CrPcF}]_n$. Whangbo and Stewart²⁵ have presented the band structure of $[\text{CrPcF}]_n$. As expected from the radial and angular dependences of the orbitals, the d_{xy} band is flat and the d_{xz} and d_{yz} bands are rather narrow. All three of these lie above the band formed by the HOMO's of adjacent phthalocyaninate rings, and, in the case of electron localization, one electron is required in each band per unit cell. As noted by Whangbo and Stewart²⁵, this electron assignment implies the presence of three unpaired electrons per chromium in $[\text{CrPcF}]_n$. This suggestion has been verified by this study.

Exchange coupling may be understood in terms of the localized description and superexchange principles. The magnetic orbitals on chromium(III) are xz , yz , and xy , and assuming a linear structure, no σ -overlap between the metal magnetic orbitals and bridging ligand orbitals results. However, the fluorine p orbital that is collinear with the Cr-F-Cr axis is properly oriented to provide a contribution to J_F by interaction with the π orbitals on a pair of adjacent chromium(III) ions. The two p orbitals normal to the Cr-F-Cr unit, p_\perp orbitals, are oriented appropriately for finite overlap with the positive linear combinations $(xz_i + xz_j)/\sqrt{2}$ and $(yz_i + yz_j)/\sqrt{2}$ (where i and j denote adjacent

chromium(III) ions). In view of the angular dependence of xz and yz , it may be expected that overlap of ligand p_z with the combinations of xz and yz will be significant. These interactions lead to large contributions to J_{AF} which are the predominant exchange interactions in fluoro-bridged $[\text{CrPcF}]_n$.

Exchange in $[\text{CrPcCN}]_n$. The electronic configuration of the cyanide ion is $(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^4(\sigma_z^b)^2$, and there are low-lying unoccupied molecular orbitals. The most important LUMO is $\pi_{x,y}^*$. Cyano-bridged chains and polymers containing the linear $\text{M}-\text{C}\equiv\text{N}-\text{M}$ unit are well known, and it is expected that $\text{Cr}-\text{C}\equiv\text{N}-\text{Cr}$ units are linear in $[\text{CrPcCN}]_n$. Assuming a linear structure, then σ_z^b is oriented properly to provide a contribution to J_F . This contribution is not expected to be very important since the electron density in σ_z^b is maximized between the carbon and nitrogen atoms, and the radial extension of the orbital in the direction of the chromium ions is not great.

The coordination of cyanide to metal ions is stabilized by dative π bonding. In this particular case, there is the possibility for dative π bonding between chromium(III) and cyanide which involves the $\pi_{x,y}^*$ orbitals of cyanide and xz , yz orbitals of chromium. This bonding interaction is much greater than the interaction between the $\pi_{x,y}^b$ orbitals and the xz , yz orbitals on chromium since the $\pi_{x,y}^b$ orbitals are concentrated between the carbon and nitrogen atoms and have little radial extension in the direction of the chromium ions. The overall ferromagnetic exchange interaction is a result of intramolecular ferromagnetic exchange between the electron in the xy orbital and those in the dative π bonding orbitals.

Electrical Conductivity. The electrical conductivity of pressed pellet samples of $[\text{CrPcF}]_n$ is $<10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature. Although linear chain compounds can be good electrical conductors, the absence of delocalization in

$[\text{CrPcF}]_n$, as indicated by the band structure of Whangbo and Stewart,²⁵ results in low conductivity. In other words, the phthalocyaninate ligands have a closed-shell electronic configuration, and the unpaired electrons are localized on the chromium ions.

The electrical conductivity of $[\text{CrPcCN}]_n$, $3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature,¹⁴ is much lower than that of the analogous iron and cobalt compounds. It may be important to note that $[\text{CoPcCN}]_n$ exhibits EPR signals at $g = 2.0028$ and $g = 2.3$, values which suggest unpaired spin density on the macrocyclic ligand as well as on cobalt. Detailed magnetic susceptibility and EPR studies on these compounds may provide information concerning the mechanism of the electrical conductivities. Such studies will be undertaken in the near future.

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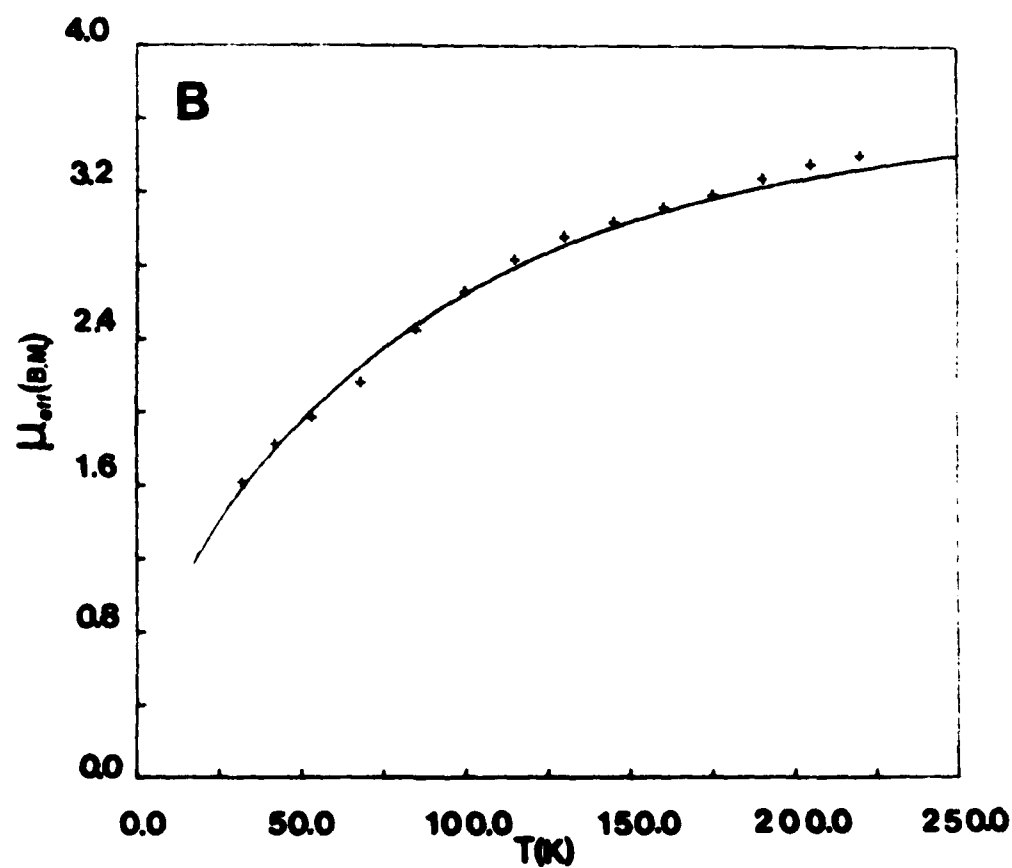
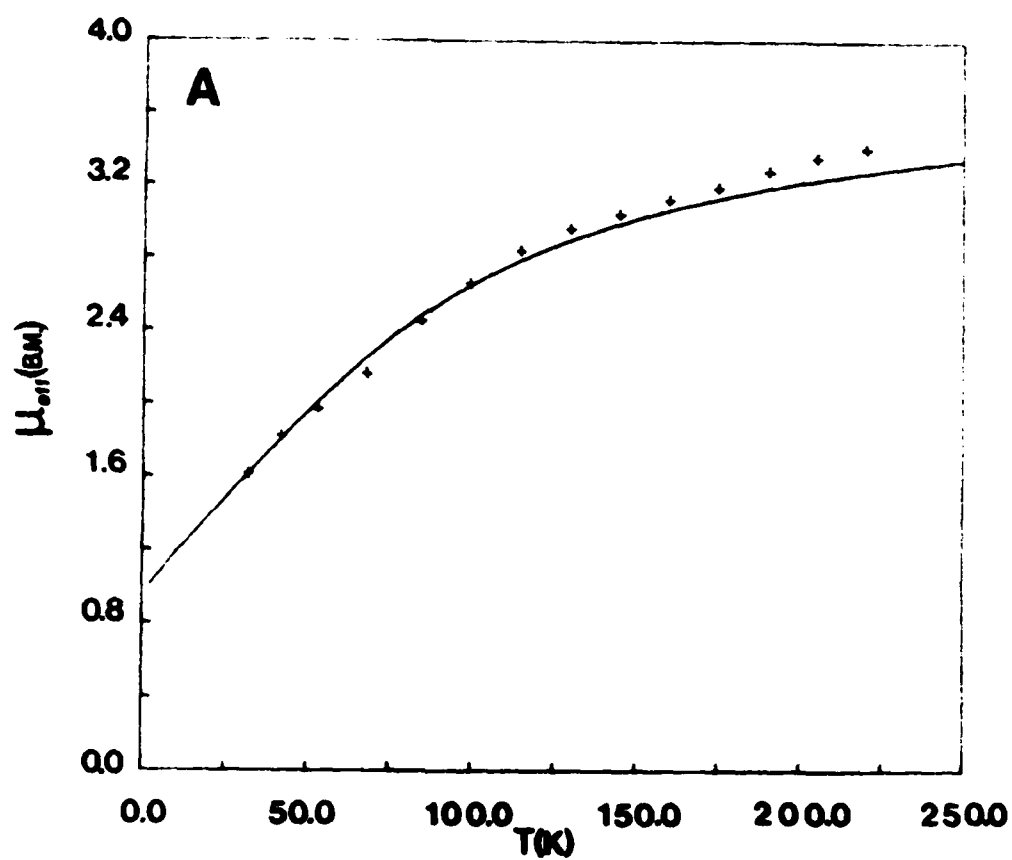
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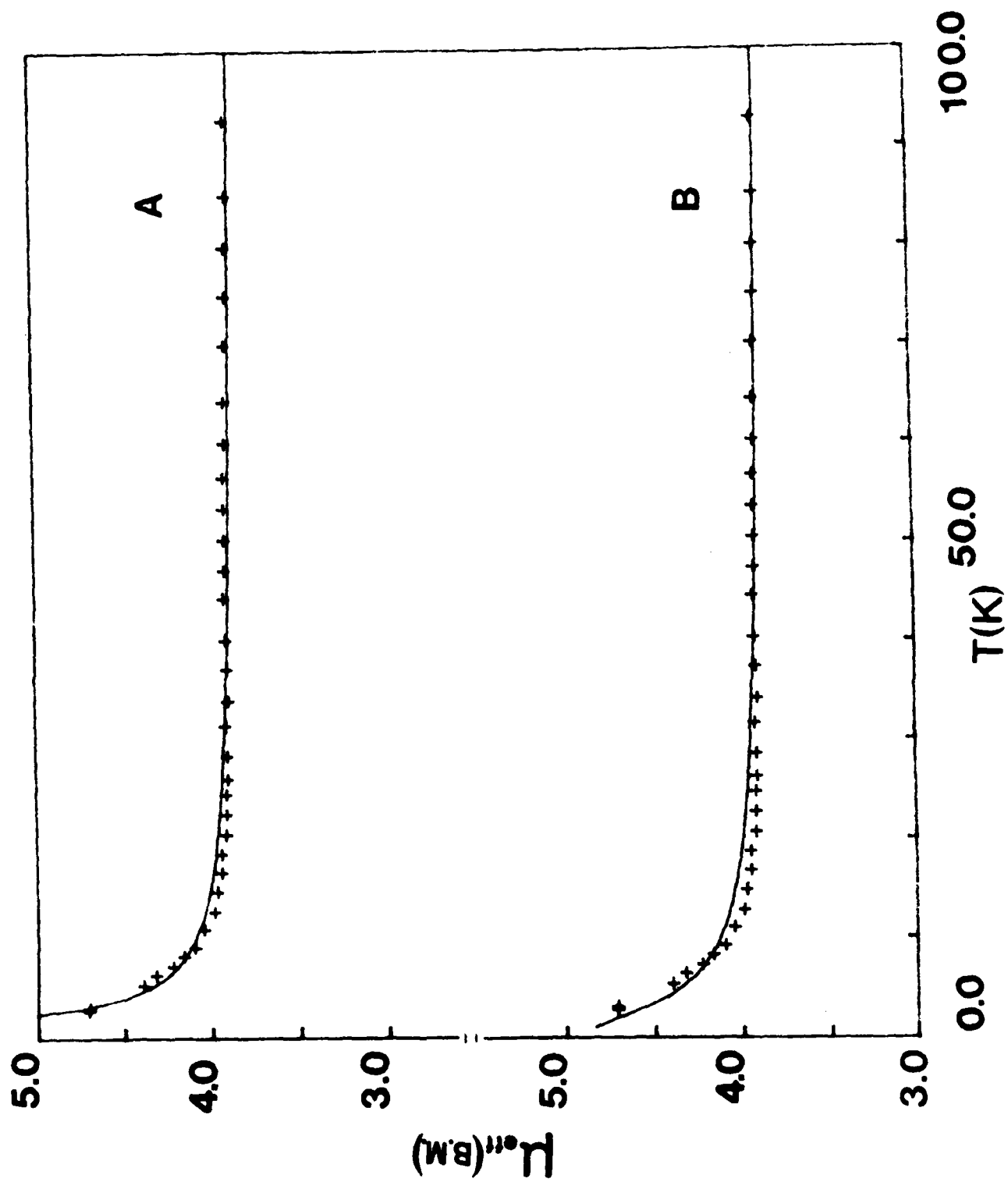
Figure Captions

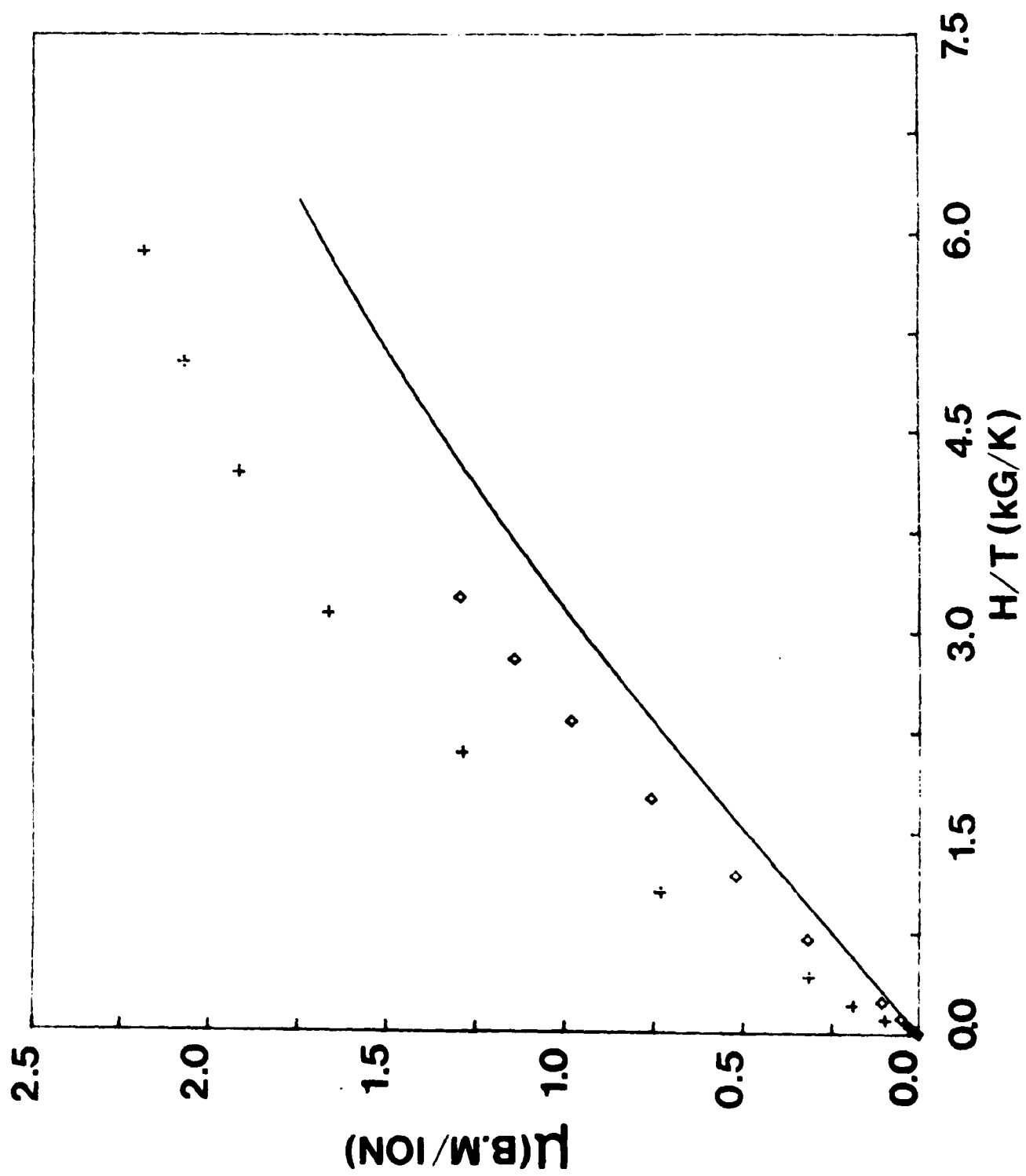
Figure 1. Temperature variation of the magnetic moment of $[\text{CrPcF}]_n$. (A) The solid line is the best fit to the data by a Heisenberg antiferromagnetic linear chain with $S = 3/2$. The best fit parameters are given in the text. (B) The solid line is the best fit to the data by a Heisenberg model for a pair of exchange coupled $S = 3/2$ ions.

Figure 2. Temperature variation of the magnetic moment of $[\text{CrPcCN}]_n$. (A) The solid line is the best fit to the scaled Heisenberg linear chain model for $S = 3/2$. The best fit parameters are given in the text. (B) The solid line is the best fit to the data by a Heisenberg model for a pair of exchange coupled $S = 3/2$ ions.

Figure 3. Magnetization data for $[\text{CrPcCN}]_n$. The solid line is the magnetization of an $S = 3/2$ system. Experimental data were collected at 2.4 K (+) and 4.2 K (x).







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